

**ANTI-FOGGING FILM, AND SUBSTRATE WITH ANTI-FOGGING FILM**

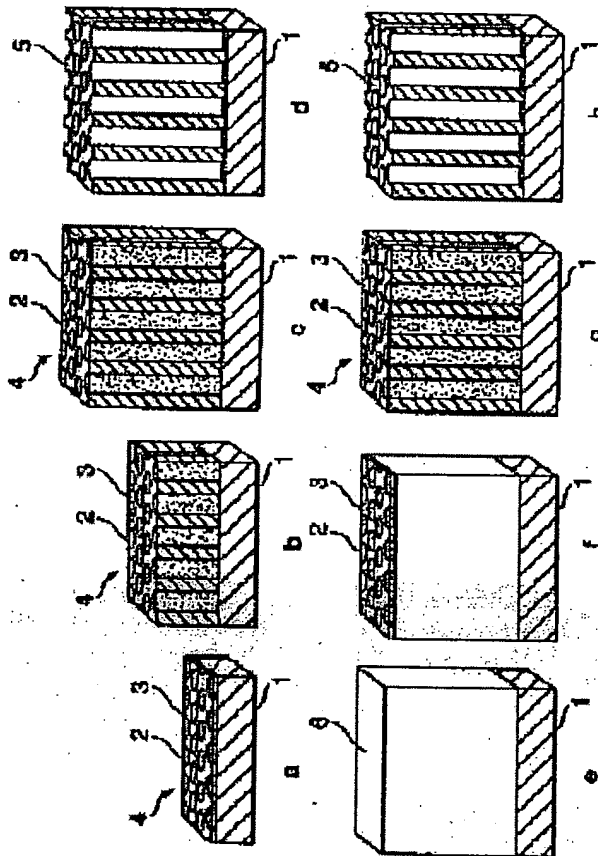
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**Abstract of JP2001261376**

**PROBLEM TO BE SOLVED:** To obtain an anti-fogging film having a high film strength and excellent adhesivity to a substrate.

**SOLUTION:** This anti-fogging film is formed by removing one-dimensionally grown columnar phases 2 from a composite film 4 consisting of a great number of the columnar phases 2 and a matrix phase 3 surrounding the columnar phases on a substrate 1 and has a great number of one-dimensionally penetrated pores enclosed by walls continuous from one surface of the film to the other surface and  $\leq 30$  deg. contact angle to water.



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CLAIMS

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## Claim(s)]

Claim 1] The anti-fogging film characterized by to be the anti-fogging film which has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side, and which are penetrated in single dimension formed on the base by removing the pillar-shaped phase which grew like a single dimension in the bipolar membrane which consists of a pillar-shaped phase of a large number which grew in single dimension, and a matrix phase which encloses it, and for the contact angle over water to be 30 degrees or less.

Claim 2] The anti-fogging film according to claim 1 with which said anti-fogging film consists of one or more sorts chosen from an oxide, carbide, the boride, the nitride, and the metal.

Claim 3] The anti-fogging film according to claim 1 or 2 whose average aperture of said pore penetrated in single dimension is 1-500nm.

Claim 4] The anti-fogging film according to claim 1, 2, or 3 whose specific surface area of said anti-fogging film is 0-2000m<sup>2</sup>/g.

Claim 5] The base with an anti-fogging film which has an anti-fogging film according to claim 1, 2, 3, or 4 on a base.

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DETAILED DESCRIPTION

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## Detailed Description of the Invention]

0001]

Field of the Invention] This invention relates to an anti-fogging film with the pore (henceforth single dimension penetration pore) penetrated in single dimension. In detail, it can use suitably as anti-fogging films for cloudy prevention, such as a windowpane, a mirror, or an optical lens front face, and is related with the anti-fogging film which has high endurance.

0002]

Description of the Prior Art] If the mirror of a bathroom or a washstand touches the air which contains a steam so much, the waterdrop of wavelength extent of light or the magnitude beyond it adheres to a front face, scattered reflection of the light will be carried out by the waterdrop, and the overcast will be produced by it. Moreover, the overcast will be produced, if the waterdrop of wavelength extent of light or the magnitude beyond it adheres to windshield insides, such as a windowpane inside of the building cooled by the open air, and an automobile, or the front face of glasses and light is scattered on it by the waterdrop. These are because minute waterdrop adheres to the glass front face which should be transparency essentially.

0003] The front face of the glass used for a mirror or an aperture shows the middle property (it is about 50-90 degrees to the contact angle of pure water) of a hydrophilic property and hydrophobicity, and the fundamental cause of this problem originates in a drop adhering to a glass front face in the shape of a semi-sphere. A metal with the wettability equivalent [ such a problem ] to glass not only to glass but water, the ceramics, or plastics of a certain kind may happen similarly.

0004] Thus, in order to solve the problem which blooms cloudy by adhesion of a drop with a minute front face, the film of a hydrophilic property was formed in the front face of glass or plastics, and the method of making fog resistance is discovered by making it not become semi-sphere-like, even if waterdrop adheres etc. has been proposed. Specifically, the approach of carrying out hydrophilization processing of the front face of glass or plastics with organic cationic surface active agents, such as A dimethyl alkylammonium chloride, the method of sticking on the front face of glass or plastics the transparency resin film which scoured B surface active agent and titanium oxide, etc. have been proposed.

0005] Moreover, porous inorganic film (an alumina, alumina-silica system, etc.) was formed in front faces, such as C glass and plastics, and the method of aiming at improvement in a hydrophilic property with surface irregularity etc. has been tried.

0006] However, in the approach of A, since the adhesion force of a surfactant was weak, when it used for a windowpane or the windshield of an automobile, there was a problem the hydrophilic effectiveness and whose antifog effectiveness a surfactant component \*\*\*\*s immediately and are lost. Moreover, by the approach of B, the surfactant component was eluted from the transparency resin film, the hydrophilic effectiveness decreased and there was a problem which a transparency resin film deteriorates in sunlight and loses transparency.

0007] The approach of C) can expect improvement in endurance to some extent compared with the approach of using the above-mentioned organic film. However, by such film, in order to raise the antifog effectiveness, when membranous porosity was made to increase, the problem to which the reinforcement of the film itself and the adhesion reinforcement of the film and a substrate become low and which carries out property top phase conflict arose in many cases.

0008] Moreover, although the approach of heating, drying or sintering is usually used after adjusting the ceramic

slurry containing impalpable powder, such as a silica and an alumina, and applying a slurry to the front face of glass or plastics with a dip method, a doctor blade method, etc. when forming the porosity inorganic film, it is difficult to arrange the pore diameter of the pore contained in the film by the film made by this approach, and it is usually that the hole which is dozens of micrometers surely exists. Thus, when the big hole existed in the film front face, there was a problem to which it becomes difficult for particles which float in air, such as tar of tobacco and various dust, to be fitted in and crowded in this hole, and to remove these in easy washing.

[0009]

[Problem(s) to be Solved by the Invention] This invention cancels the above-mentioned fault which the conventional technique has, and membranous reinforcement is high and it aims at offer of the anti-fogging film which is excellent also in adhesion with a base, and a base with an anti-fogging film. This invention aims at offer of said anti-fogging film to which dirt tends to fall, and a base with an anti-fogging film again.

[0010]

[Means for Solving the Problem] The inside of the bipolar membrane which this invention becomes from the pillar-shaped phase of a large number which grew in single dimension on the base, and the matrix phase which encloses it, It is the anti-fogging film which has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side, and which are penetrated in single dimension formed by removing the pillar-shaped phase which grew in single dimension, and the anti-fogging film characterized by the contact angle over water being 30 degrees or less is offered.

[0011] In this invention, a matrix phase serves as an ingredient which constitutes an anti-fogging film, and this matrix phase is a substantia-compacta object. The anti-fogging film of this invention is formed in two steps of processes. That is, the pillar-shaped phase which formed the bipolar membrane which consists of a pillar-shaped phase of a large number which grew in single dimension, and a matrix phase which encloses it, next grew like a single dimension in the bipolar membrane on the second stage story is removed by etching, and only a matrix phase is made to remain on a first stage story.

[0012] As an approach of forming bipolar membrane in a first stage story How to form directly the bipolar membrane which consists of a pillar-shaped phase which grew in single dimension, and a matrix phase which encloses it by the physical forming-membranes method (henceforth the first formation approach of bipolar membrane), The amorphous precursor film is first formed on a base, and then the approach (henceforth the second formation approach of bipolar membrane) of forming the bipolar membrane which consists an eutectic reaction of a lifting, and the pillar-shaped phase which grew in single dimension by this and the matrix phase which encloses it is listed by heat treatment.

[0013] Drawing 1 is the mimetic diagram showing the procedure which forms the anti-fogging film of this invention. a-d shows among drawing the procedure which forms the anti-fogging film of this invention using the first formation approach of bipolar membrane. The condition in which a formed the bipolar membrane 4 which consists of a pillar-shaped phase 2 and a matrix phase 3 by the physical forming-membranes method on the base 1 (first stage), The condition (middle) in which b formed bipolar membrane 4 similarly, the condition in which formation of bipolar membrane 4 ended c, and d remove the pillar-shaped phase 2 which grew in single dimension by selective etching, and the condition that the anti-fogging film 5 of this invention was formed is shown, respectively.

[0014] Moreover, e-h shows the procedure which forms the anti-fogging film of this invention using the second formation approach of bipolar membrane. The condition in which the amorphous precursor film 6 with which e contains transition metals was formed on the base 1, An eutectic reaction interface moves the condition that, as for f, eutectic structure was formed in the film front face of heat treatment, and g, to the film and a substrate interface by oxygen diffusion from a front face. The eutectic structure which consists of a pillar-shaped phase (transition-metals oxide crystal) 2 which finally grew in single dimension, and a matrix phase 3 which encloses it is formed. The condition which was able to do bipolar membrane 4, and h remove the pillar-shaped phase 2 which grew in single dimension by selective etching, and the condition that the anti-fogging film 5 of this invention was formed is shown, respectively.

[0015] In the first formation approach of bipolar membrane, a spatter, vacuum deposition, a CVD method, the laser ablation method, a molecular beam epitaxy method, etc. are mentioned as a physical forming-membranes method which forms bipolar membrane. Also in this, in addition to that it is easy to obtain the precise film and the film with high adhesion with a base being obtained, the spatter is excellent in mass-production nature or large area membrane formation nature, and especially desirable.

0016] Although it is not limited especially as an approach of constituting a target using the ingredient which forms a pillar-shaped phase, and the ingredient which forms a matrix phase when forming bipolar membrane by the sputter, what mixed the powder of the ingredient which forms a pillar-shaped phase, and the powder of the ingredient which forms a matrix phase can be used as a target.

0017] Moreover, many wafers with a magnitude of about several mm which consists of an ingredient which forms a matrix phase on the target which consists of an ingredient which forms a pillar-shaped phase are arranged, and what was used as the multicomponent target can be used suitably. Many wafers with a magnitude of about several mm which consists of an ingredient which forms a pillar-shaped phase on the target which consists of an ingredient which forms a matrix phase on the contrary are arranged, and what was used as the multicomponent target can be used suitably.

0018] When producing bipolar membrane by the first formation approach of bipolar membrane, as a combination of the ingredient of a pillar-shaped phase and a matrix phase, the ingredient of a pillar-shaped phase and the ingredient of a matrix phase should just be the combination which starts phase separation at the time of film production. In this invention, the metal or alloy which is the metal which is easy to grow in the shape of a column as an ingredient of a pillar-shaped phase, and dissolves in an acid, alkali, etc. easily and which binding energy with the ingredient of a matrix phase is easy to be returned to it small in order to use the matrix phase which encloses a pillar-shaped phase for the pore part after etching a pillar-shaped phase as a residual phase is desirable.

0019] One or more sorts chosen from the alloy which makes a principal component alkaline earth metal, such as an alloy and Mg, and it which make a principal component 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and it in consideration of the ease of the handling at the time of a sputter practical as an example of the ingredient of a pillar-shaped phase are mentioned. In addition, aluminum, In, Sn, Pb, etc. can be used.

0020] as the example of the matrix phase used as a residual phase -- metals, such as nitrides, such as borides, such as carbide, such as oxide, such as a silica, an alumina, a titania, a mullite, cordierite, a spinel, a zeolite, and forsterite, silicon carbide, titanium carbide, and zirconium carbide, titanium boride, zirconium boride, and boron carbide, silicon nitride, titanium nitride, and zirconium nitride, and Cr, nickel, Cu, Au, aluminum, Pt, -- since -- one or more sorts chosen are mentioned.

0021] In the first formation approach of bipolar membrane, the detailed organization for which the matrix phase enclosed the surroundings of the pillar-shaped phase which grew in single dimension is formed by controlling the mixing ratio and membrane formation conditions of an ingredient of a pillar-shaped phase and a matrix phase. For example, when forming bipolar membrane by the sputter, the average diameter of the pillar-shaped phase which grows changes with the volume fraction and membrane formation conditions (Ar gas pressure at the time of a sputter) of a pillar-shaped phase and a matrix phase.

0022] Since the diameter of single dimension penetration pore is mostly in agreement with the diameter of the pillar-shaped phase which grows in single dimension, the average aperture of the single dimension penetration pore of the anti-fogging film of this invention finally obtained after etching is changeable with the mixing ratio and membrane formation conditions of an ingredient of a pillar-shaped phase and a matrix phase (Ar gas pressure, substrate temperature, etc. at the time of a sputter). For example, in the case of Co-SiO<sub>2</sub> system, to the particle size of Co in the film which produced the film with 2Pa Ar gas pressure being 8nm, when a film is produced with 8Pa Ar gas pressure, it is checked that the particle size of Co is set to about 40nm.

0023] In the second formation approach of bipolar membrane, plating etc. can be used for solution methods, such as the physical forming-membranes methods, such as a sputter, vacuum deposition, a CVD method, the laser ablation method, and a molecular beam epitaxy method, and a sol-gel method, the spray pyrolysis method or the applying method, and a pan as an approach of forming the amorphous precursor film. Also in this, in addition to that it is easy to obtain the precise film and the film with high adhesion with a base being obtained, the sputter is excellent in mass-production nature or large area membrane formation nature, and especially desirable.

0024] Although it is not limited especially as an approach of constituting a target using the ingredient which forms a pillar-shaped phase, and the ingredient which forms a matrix phase when forming the amorphous precursor film by a sputter etc., what mixed the powder of the ingredient which forms a pillar-shaped phase, and the powder of the ingredient which forms a matrix phase can be used as a target. For example, when forming the amorphous precursor film of a Fe-Si-O system, what mixed FeO powder and SiO<sub>2</sub> powder can be used as a target.

0025] In the second formation approach of bipolar membrane, there are the as other metallic element and the oxygen as a combination of an element which are contained in the amorphous precursor film formed first as transition metals.

Be [ what is necessary / just although it dissociates with other metals contained in the film and becomes a separate compound phase after heat treatment as an example of transition metals ] rare earth elements, such as an alloy which uses 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and these metals as a principal component in consideration of the ease of the handling at the time of heat treatment etc., and the other multiple-valued cations Ce, Nd, Sm, and Er, -- since -- one or more sorts chosen are mentioned.

[0026] What is necessary is just not to react with transition metals at the time of heat treatment continuously performed as metallic elements other than transition metals. Since this metallic element serves as a component which constitutes the film which serves as a matrix phase which encloses a pillar-shaped phase (transition-metals compound needle crystal) at the time of heat treatment, and has single dimension penetration pore after etching, it is chosen by the membranous use purpose. For example, Si, aluminum, Mg, Zr, Sn, In, etc. are mentioned.

[0027] When carrying out spatter membrane formation of the amorphous precursor film, the diameter of the pillar-shaped phase which grows in single dimension by heat-treatment performed behind changes with the Ar gas pressure at the time of a spatter. For example, if the film which produced the film with 2Pa Ar gas pressure is heat-treated at 600 degrees C in the case of the film of a Fe-Si-O system, hematite ( $\text{Fe}_2\text{O}_3$ ) with a diameter of about 4nm deposits, but when a film is produced with 8Pa Ar gas pressure, if same processing is performed, hematite with a diameter of about 20nm deposits. Since the diameter of single dimension penetration pore is mostly in agreement with the diameter of the pillar-shaped phase which grows in single dimension, the average aperture of the single dimension penetration pore of the anti-fogging film of this invention finally obtained after etching is controllable by membrane formation conditions (Ar gas pressure at the time of a spatter).

[0028] The amorphous precursor film containing transition metals, the other metal, and oxygen is heat-treated, and the eutectic decomposition reaction in which a transition-metals oxide and the oxide of the other metal carry out a separation deposit is made to cause in the second formation approach of bipolar membrane. It is important for the two phase deposit from this amorphous phase to happen from a film front face to coincidence moreover. What is necessary is just the conditions from which an eutectic decomposition reaction occurs as processing conditions when heating. namely, the temperature from which an eutectic decomposition reaction occurs about temperature -- in addition -- and a reaction should just be the temperature which advances at sufficient rate. Specifically, the temperature of about 400-650 degrees C is desirable.

[0029] In order to trigger an eutectic decomposition reaction, it is necessary to change the valence of transition metals. Two, the case where the amorphous precursor film is processed in the ambient atmosphere of an oxidizing quality, and the method of processing in the ambient atmosphere of reducibility, are possible as this approach. In the case of the eutectic reaction of an oxide, if it processes by reducing atmosphere, ununiformity nucleation is carried out and uniform eutectic structure may not be formed. In this case, uniform eutectic structure can be formed by heat-treating under an oxidizing atmosphere.

[0030] On a second stage story, using an acid or alkali, only the pillar-shaped phase extended in single dimension is etched alternatively, and is removed from the bipolar membrane formed on the first stage story. The thing suitable for removing alternatively only pillar-shaped phases, such as a sulfuric acid, a hydrochloric acid, a nitric acid, oxalic acid, and an acetic acid, as an acid used by this etching processing is chosen. For example, only metal cobalt is completely removable from the metal cobalt silica bipolar membrane produced by the first formation approach of bipolar membrane only by processing for several minutes in the nitric-acid water solution of 0.1 mols / L removing metal cobalt.

[0031] Moreover, in the case of the bipolar membrane of the Fe-Si-O system formed by the second formation approach of bipolar membrane, the hematite extended in single dimension can carry out selective etching by immersing the film in the water solution of a hydrochloric acid to being meltable, at the hydrochloric-acid water solution of about 6 mol/L, since the silica is insoluble in this solution.

[0032] It is the anti-fogging film which has the pore of a large number which were surrounded with the wall which the anti-fogging film of this invention is formed as mentioned above, and continues from one membranous front face to the front face of another side, and which are penetrated in single dimension, and the contact angle over water is the film 30 degrees or less. Antifog effectiveness with the contact angle sufficient by 30-degree \*\* over water is not acquired.

[0033] Although the anti-fogging film of this invention consists of one or more sorts chosen from an oxide, carbide, the boride, the nitride, and the metal and it is chosen according to an application, the viewpoint of endurance, reinforcement, chemical stability, the ease of forming, etc. to an oxide is the most desirable. Moreover, from a fog

resistance viewpoint, a silica is desirable.

[0034] Moreover, as for the average aperture of the pore penetrated in single dimension in the anti-fogging film of this invention, it is desirable that it is 1-500nm. In less than 1nm, sufficient antifog effectiveness is not acquired, antifog effectiveness sufficient in 500nm \*\* is not acquired, and also membranous reinforcement or adhesion with a base may also fall.

[0035] Furthermore, as for the specific surface area of the anti-fogging film of this invention, it is desirable that it is 20-2000m<sup>2</sup>/g. Under by 20m<sup>2</sup>/g, sufficient antifog effectiveness may not be acquired and sufficient film reinforcement may not be obtained at 2000m<sup>2</sup>/g \*\*.

[0036] This invention offers the base with an anti-fogging film which has said anti-fogging film on a base again. When a substrate or films, such as glass, ceramics, a metal, and plastics, can be used as a base which forms the anti-fogging film of this invention when using the first formation approach of bipolar membrane, and using the second formation approach of bipolar membrane, a substrate or films, such as glass, ceramics, and a heat-resistant metal, can be used.

[0037] Oxidation-resistant alloys, such as stainless steel which consists of Fe, nickel, Cr, V, etc. as a heat-resistant metal, and Hastelloy, are suitable. Moreover, what is necessary is just to form the bipolar membrane by the first formation approach, or the amorphous precursor film by the second formation approach directly, if surface irregularity is not so intense when forming the anti-fogging film of this invention on the base which has irregularity on front faces, such as a porosity ceramic substrate. If a front face is ground, it is made smooth and the anti-fogging film of this invention is formed on a smooth base front face after filling up the irregularity on the front face of a base with the ingredient of resin and others when [ that the irregularity on the front face of a base is intense ] direct formation of the film of a first stage story is difficult, sufficient adhesion reinforcement is securable. The anti-fogging film of this invention can consist of various presentations. The anti-fogging film of this invention is suitable for the anti-fogging film used for the windshield of a car, the windowpane of a building, a mirror, an optical lens, etc.

[0038]

[Function] Since the pore which continues from a film front face exists to the interior of the film, the anti-fogging film of this invention has a high hydrophilic property in extent which the waterdrop adhering to a front face permeates to the interior of the film, and shows the antifog effectiveness practically.

[0039] Furthermore, since the continuous matrix phase encloses the surroundings of the penetration pore of a single dimension, the anti-fogging film of this invention has theoretically large film reinforcement compared with the former of a certain porosity inorganic film, and its adhesion with a base is also good. By the film of this invention, the matrix which encloses single dimension penetration pore depends that film reinforcement is large on it being really which continued completely a moldings to the conventional porosity inorganic anti-fogging film combining a ceramic particle closely by sintering etc.

[0040] Moreover, also about adhesion with a substrate, if the bipolar membrane (including the amorphous precursor film by the second formation approach) of a first stage story is formed by a spatter etc., the high film of especially adhesion will be obtained. Moreover, although the problem to which the reinforcement of the film itself and the adhesion reinforcement of the film and a substrate become low and which carries out property top phase conflict arose in many cases when membranous porosity was made to increase in order that the conventional porosity inorganic film might raise the antifog effectiveness. In the anti-fogging film of this invention, maintaining the high antifog effectiveness, both can make membranous reinforcement and adhesion with a base high, and the anti-fogging film which has fog resistance and high endurance can be realized.

[0041]

[Example] (Example 1) The bipolar membrane which consists of two phases of metals Co and SiO<sub>2</sub> was formed on the soda lime glass substrate with a thickness of 1.2mm using the first formation approach of bipolar membrane. On the occasion of the spatter, the multicomponent target which placed SiO<sub>2</sub> tip of 5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of SiO<sub>2</sub> chip was adjusted so that 20% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10<sup>-4</sup> Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 600W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.25 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation. In addition, the substrate periphery gave a mask and did not form the film.

[0042] Thus, as a result of observing Co-SiO<sub>2</sub> formed bipolar membrane by TEM (transmission electron microscope),

Co crystal grain child with a mean particle diameter of about 10nm was growing in the shape of a column, and it was checked that the amorphous SiO<sub>2</sub> matrix phase encloses the surroundings of it.

[0043] Co-SiO<sub>2</sub> bipolar membrane of 500nm of thickness formed by the above-mentioned approach as a second stage story was etched into the nitric-acid water solution of 0.1 mol/L by being immersed for 5 minutes. As a result of observing the film after removing the pillar-shaped phase of Co by etching from Co-SiO<sub>2</sub> bipolar membrane by SEM (scanning electron microscope), Co pillar-shaped phase was eluted and it was checked that the SiO<sub>2</sub> matrix phase remains.

[0044] Drawing 2 is an isothermal adsorption-and-desorption curve in the liquid nitrogen temperature of the anti-fogging film formed as mentioned above. It has much pores whose anti-fogging films with which adsorption and desorption of clear nitrogen gas were seen and obtained from drawing in the differential pressure  $(P/P_0) = 0.6$  neighborhood are the diameters of about 10nm, and it turns out that the specific surface area of the wall of a hole is about 1000m<sup>2</sup>/g (extent equivalent to activated carbon).

[0045] Moreover, when the waterdrop of pure water with a diameter of about 1mm was dropped at the front face of the obtained anti-fogging film and the contact angle was measured, it was about 15 degrees. Moreover, after having put the obtained anti-fogging film into the refrigerator the whole substrate, holding for 1 hour and cooling at about 5 degrees C, when it took out and exhalation was blown, minute waterdrop adhered to the glass front face which does not have the film in a part with the film to the overcast not arising, the overcast arose, and it became opaque.

[0046] When the Taber abrasion resistant test investigated the endurance of an above-mentioned anti-fogging film, change was not looked at by the contact angle of water, fog resistance ability, transparency, etc. even if it rotated 1000 times. In addition, the Taber abrasion resistant test is commercial CS10 mold Taber wearing-of-die ring and JIS. It carried out by applying a 500g load, rotating 1000 times by 60rpm using the abrasive paper of quality equivalent to the abrasive paper of AA of No. 180 specified to R6252, and wearing the film. The same is said of the Taber abrasion resistant test in the following examples.

[0047] (Example 1 of a comparison) After applying to a soda lime glass substrate front face the coating liquid which added and carried out viscosity control of the hydrochloric acid to the ethyl silicate water solution which distributed the polystyrene particle (mean particle diameter of 0.06 micrometers), it heated at about 400 degrees C, and the porosity silica film of 500nm of thickness was formed. When the same Taber abrasion resistant test as an example 1 investigated endurance, in 1000 times, a part of film exfoliated and transparency was spoiled.

[0048] (Example 2) Co-SiO<sub>2</sub> bipolar membrane of 500nm of thickness was formed like the example 1 except having made the membrane formation rate into about 0.3 nm/sec. Like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1, the structure inside this Co-SiO<sub>2</sub> bipolar membrane found that the mean particle diameter of Co crystal was large with about 20nm in this case, although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase.

[0049] The sample of 500nm of thickness produced by the above-mentioned approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co pillar-shaped phase was carried out. Co pillar-shaped phase was eluted like the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 13 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0050] (Example 3) Co-SiO<sub>2</sub> bipolar membrane was formed on the soda lime glass substrate with a thickness of 1.2mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to  $5 \times 10^{-4}$  Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 8Pa. Membrane formation rates are about 0.6 nm/sec, and heated substrate temperature at 200 degrees C at the time of membrane formation.

[0051] Like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1, the structure inside this Co-SiO<sub>2</sub> bipolar membrane found that the mean particle diameter of Co crystal was large with about 100nm in this case, although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase.

[0052] The sample of 1500nm of thickness produced by the above-mentioned approach was immersed in the nitric-acid water solution of 0.1 mol/L for 15 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 12 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

1053] (Example 4) Co-SiO<sub>2</sub> bipolar membrane was formed on the Hastelloy plate with a thickness of 2mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.35 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

1054] Although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 10nm in this case. The sample of 800nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 10 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 100m<sup>2</sup>/g and 12 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to example 1 by the experiment which blows exhalation.

1055] (Example 5) Co-SiO<sub>2</sub> bipolar membrane was formed on the alumina-ceramics substrate with a thickness of 1mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

1056] Although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 9nm in this case. The sample of 700nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 10 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 100m<sup>2</sup>/g and 16 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to example 1 by the experiment which blows exhalation.

1057] (Example 6) Co-SiO<sub>2</sub> bipolar membrane was formed on the polyethylene film sheet with a thickness of 1.8mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.2 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

1058] Although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 15nm in this case. The sample of 200nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 100m<sup>2</sup>/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to example 1 by the experiment which blows exhalation.

1059] (Example 7) After applying the epoxy resin on the porosity silica plate with a thickness of 2mm and stiffening the substrate front face was ground with diamond polish equipment, and the smooth polished surface was acquired. On this substrate, Co-SiO<sub>2</sub> bipolar membrane was formed as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.35 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

1060] Although the amorphous SiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 9nm in this case. The sample of 300nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution

removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 8 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0061] (Example 8) On soda lime glass with a thickness of 1.2mm, Co-TiO<sub>2</sub> bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed TiO<sub>2</sub> tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of TiO<sub>2</sub> chip was adjusted so that 30% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.4 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0062] Although the amorphous TiO<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-TiO<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 8nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the TiO<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0063] moreover, the place which heated among air TiO<sub>2</sub> amorphous film obtained after etching at 600 degrees C for 1 hour -- the anatase of a crystalline substance -- changing -- in addition -- and a membranous specific surface area was hardly changing.

[0064] (Example 9) On soda lime glass with a thickness of 1.2mm, Co-SiC bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed the SiC tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of a SiC chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0065] Although the amorphous SiC matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-SiC bipolar membrane, the mean particle diameter of Co crystal was about 6nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiC matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0066] (Example 10) On soda lime glass with a thickness of 1.2mm, Co-Si<sub>3</sub>N<sub>4</sub> bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed Si<sub>3</sub>N<sub>4</sub> tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of Si<sub>3</sub>N<sub>4</sub> chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0067] Although the amorphous Si<sub>3</sub>N<sub>4</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-Si<sub>3</sub>N<sub>4</sub> bipolar membrane, the mean particle diameter of Co crystal was about 6nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the Si<sub>3</sub>N<sub>4</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to

in example 1 by the experiment which blows exhalation.

0068] (Example 11) On soda lime glass with a thickness of 1.2mm, Co-Cr bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed Cr tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of Cr chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to  $5 \times 10^{-4}$  to  $4 \times 10^{-4}$  Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

0069] although, as for the structure inside this Co-Cr bipolar membrane, the matrix phase which consists of the Cr crystal aggregate encloses the surroundings of Co columnar crystal particle (pillar-shaped phase) like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 -- in this case -- the mean particle diameter of Co crystal -- about 6nm it was. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and Cr matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

0070] (Example 12) On soda lime glass with a thickness of 1.2mm, Co-ZrB<sub>2</sub> bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed the ZrB<sub>2</sub> ceramic tip of 1cm angle on the metal Co target with a diameter of 15.24cm was used. The amount of a ZrB<sub>2</sub> ceramic chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to  $5 \times 10^{-4}$  to  $4 \times 10^{-4}$  Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 600W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.38 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

0071] Although the amorphous ZrB<sub>2</sub> matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO<sub>2</sub> bipolar membrane obtained in the example 1 as for the structure inside this Co-ZrB<sub>2</sub> bipolar membrane, the mean particle diameter of Co crystal was about 10nm in this case. The sample of 450nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the ZrB<sub>2</sub> matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m<sup>2</sup>/g and 22 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

0072] (Example 13) The amorphous precursor film which consists of three components of Fe-Si-O was formed by the spatter on the heat-resisting glass (Corning #7059) substrate with a thickness of 1.0mm. What mixed and sintered Fe<sub>2</sub>O<sub>3</sub> powder and SiO<sub>2</sub> powder at 70% and 30% of a rate by the volume ratio in the spatter, respectively was used for the target. After exhausting a vacuum tub up to  $5 \times 10^{-4}$  to  $4 \times 10^{-4}$  Pa, argon gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2Pa, the RF of 4.4 W/cm<sup>2</sup> was inputted, and the plasma was generated. The membrane formation rates at this time were about 0.2 nm/sec.

0073] When the amorphous precursor film which formed membranes was observed by SEM, the amorphous film with thickness of about 120nm was formed on the glass substrate. Defects, such as a crack and pore, were not seen in the amorphous film, but the very precise film was formed. Then, this amorphous film was heat-treated at 600 degrees C in air for 2 hours. When Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> bipolar membrane formed of heat-treatment was observed by TEM, it was checked that the needlelike hematite (Fe<sub>2</sub>O<sub>3</sub>) crystal extended in single dimension and the silica (SiO<sub>2</sub>) which encloses the surroundings of it form eutectic structure. The hematite crystal was extended at right angles to a film front face toward the interface with a substrate from the film front face, and the diameter was about 4nm.

0074] Finally, it was immersed in the hydrochloric-acid water solution of about 6 mol/L at the room temperature the whole substrate for 48 hours, and only hematite removed the film heat-treated by the above-mentioned approach. When the cross section of the anti-fogging film which removed hematite and was able to do it was observed by TEM, an amorphous silica matrix and the penetration pore extended in single dimension were observed. The diameter of penetration pore is the almost same 4nm as the diameter of the hematite before acid treatment, and it was checked that this penetration pore exists in the silica film. The contact angles over a membranous specific surface area and pure water are about 800m<sup>2</sup>/g and 8 degrees, respectively, and it was checked that there is the antifog effectiveness almost

equivalent to an example 1 by the experiment which blows exhalation.

[0075] (Example 14) The amorphous precursor film which consists of three components of Fe-Si-O was formed by the sputter on the heat-resisting glass (Corning #7059) substrate with a thickness of 1.0mm. What mixed and sintered  $3\text{OFe}_4$  powder and  $\text{SiO}_2$  powder at 70% and 30% of a rate by the volume ratio in the sputter, respectively was used for the target. After exhausting a vacuum tub up to  $5 \times 10^{-4}$  Pa, argon gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 8Pa, the RF of 4.4 W/cm<sup>2</sup> was inputted, and the plasma was generated. The membrane formation rates at this time were about 0.1 nm/sec.

[0076] When the amorphous precursor film which formed membranes was observed by SEM, the almost same amorphous film as an example 13 was formed by about 80nm in thickness on the glass substrate. Defects, such as a crack and pore, were not seen in the amorphous film, but the very precise film was formed. Then, this amorphous film was heat-treated at 600 degrees C among air for 2 hours. When  $\text{Fe}_2\text{O}_3$ - $\text{SiO}_2$  bipolar membrane formed of heat-treatment was observed by TEM, the needlelike hematite extended in single dimension and the silica which encloses the surroundings of it formed eutectic structure like the example 13. The hematite crystal was extended at right angles to a film front face toward the interface with a substrate from the film front face, and the diameter was about 20nm.

[0077] Finally, it was immersed in the hydrochloric-acid water solution of about 6 mol/L at the room temperature the whole substrate for 48 hours, and only hematite removed the film heat-treated by the above-mentioned approach. When gazed at the detailed organization of a film cross section by TEM, it was checked that the penetration pore of the almost same diameter as the diameter of the hematite before acid treatment exists in the silica film. The contact angles over a membranous specific surface area and pure water are about 1200m<sup>2</sup>/g and 5 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0078] (Example 2 of a comparison) The amorphous precursor film obtained in the example 13 was heat-treated at 800 degrees C among air for 1 hour. the result of having observed the film after heat-treatment by TEM -- a hematite crystal -- not needlelike -- the diameter of about 10nm -- it is spherical, and it deposited so that it might be wrapped in a silica matrix. Then, although the film heat-treated by the above-mentioned approach was immersed in the hydrochloric-acid water solution of about 6 mol/L the whole substrate, also 100 hours after, no hematite crystals were able to be removed.

[0079]

[Effect of the Invention] Holding high fog resistance ability, since the anti-fogging film of this invention has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side and which are penetrated in single dimension, its membranous reinforcement is high and it is excellent also in adhesion with a base. Moreover, the anti-fogging film of this invention can be applied to the base of varieties, and can consist of various presentations.

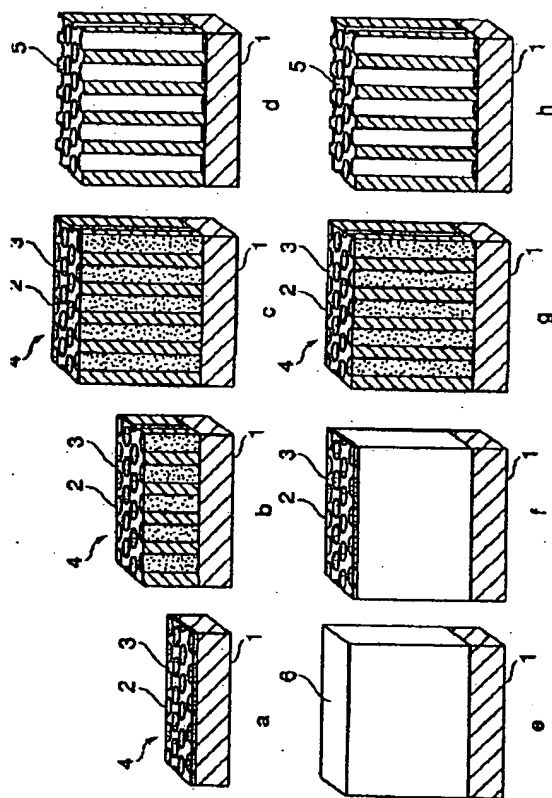
[0080] Moreover, the diameter of the pore contained in the anti-fogging film of this invention has gathered mostly in about 1-500nm, and an about dozens of micrometers huge hole does not exist. Therefore, particles which float in air, such as tar of tobacco and various dust, fit in, and are not crowded, and these can be removed by easy washing.

[0081] When the anti-fogging film of this invention uses an oxide, carbide, a boride, and a nitride as a principal component, it is suitable for anti-fogging films for cloudy prevention, such as a mirror, a structural windowpane, a windshield of an automobile, or an optical lens front face, etc. Moreover, when using metals, such as Cr, nickel, Cu, Au, aluminum, and Pt, as a principal component, it is suitable for a reflecting mirror, the surface coat of mirror on a curved road, the anti-fogging film for coatings for infrared reflection, etc.

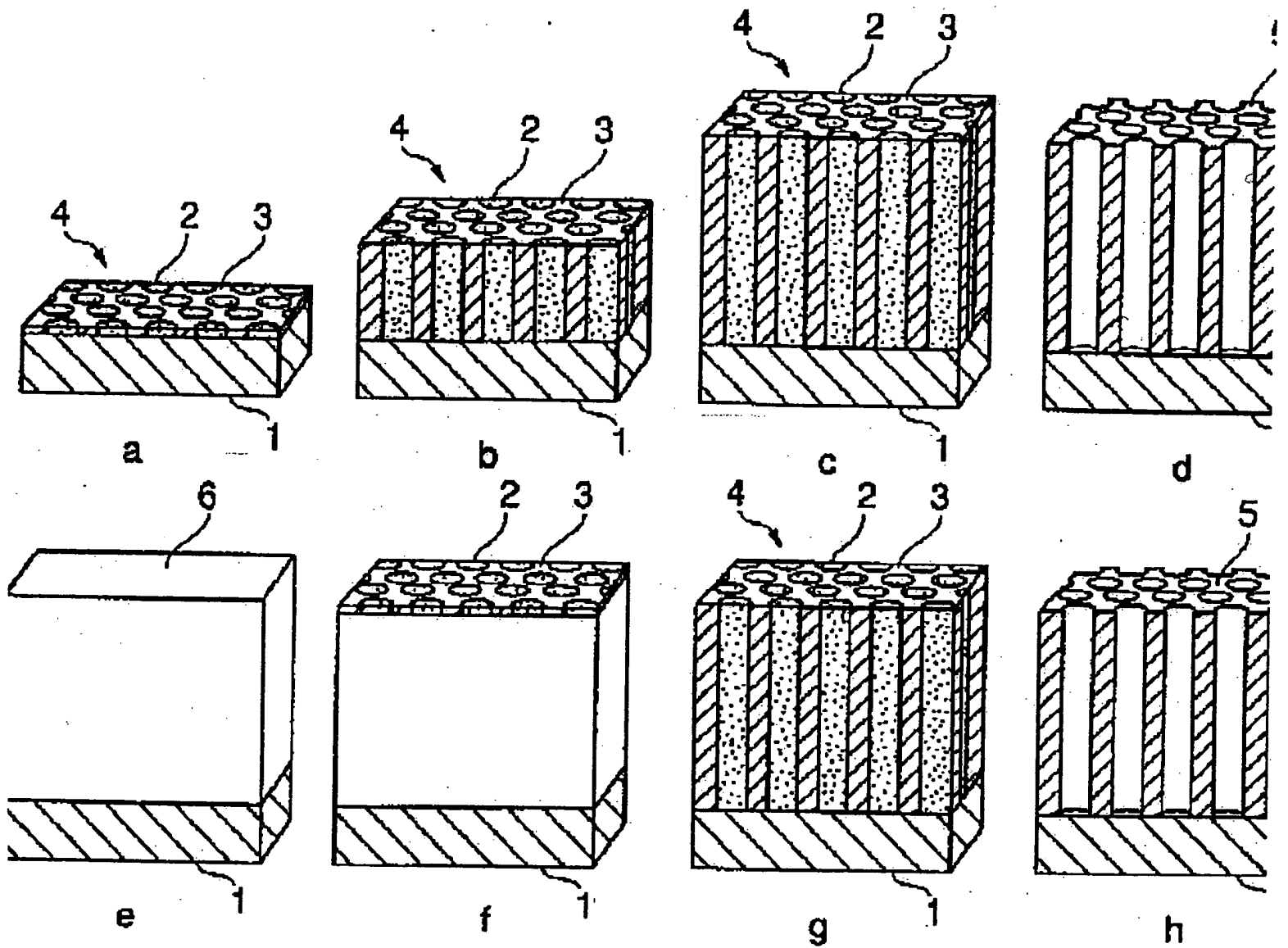
[0082] Since the anti-fogging film of this invention has the pore penetrated from a front face to the interior of the film and has a big specific surface area, it can add an antifouling function by photodissociating the organic substance which added the catalyst function and the catalyst support function, and adhered to the front face etc., and can also use it as the film with which fog resistance continues indefinitely.

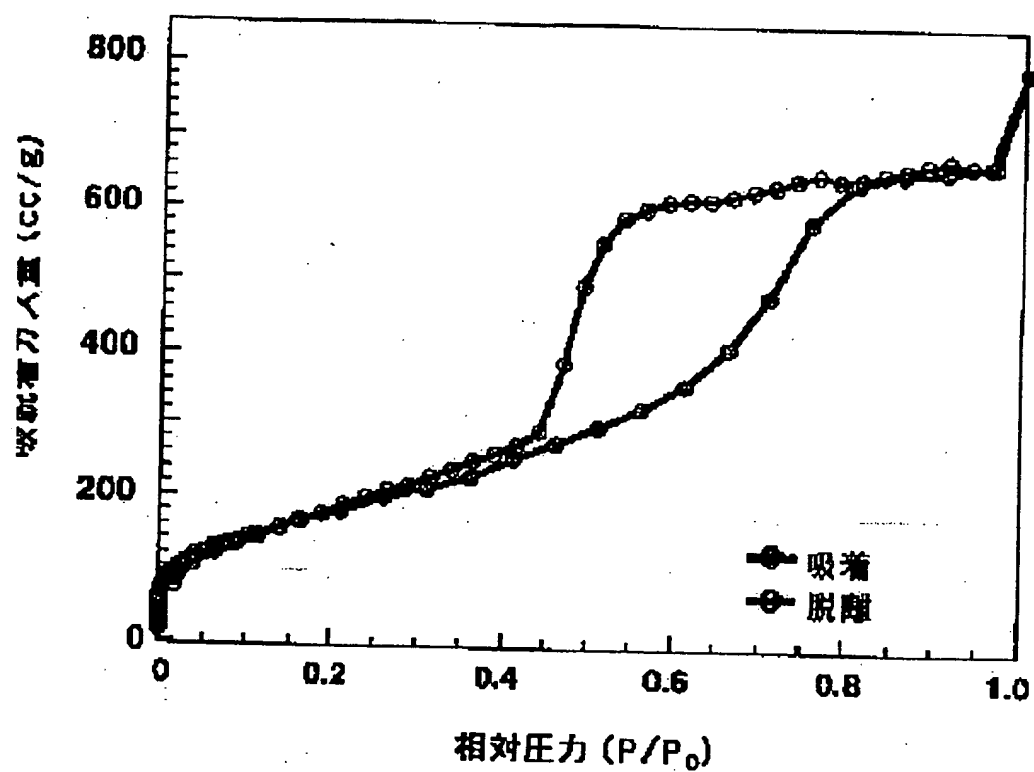
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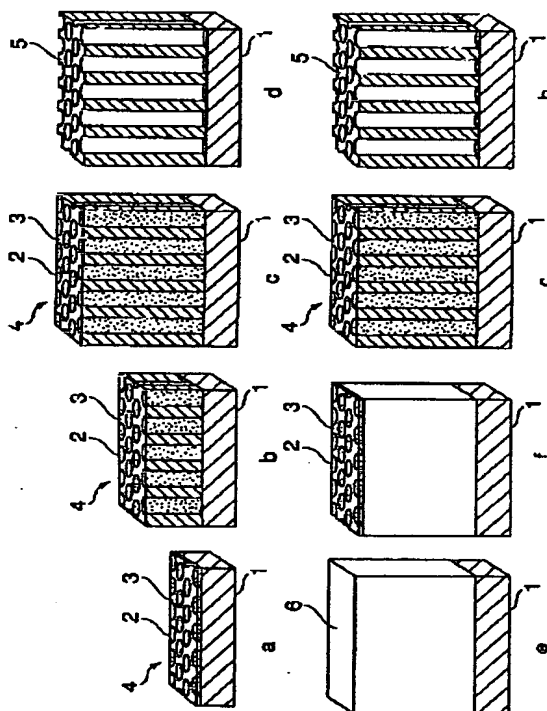
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(54) 【発明の名称】 防曇膜および防曇膜付き基体

(57) 【要約】

【課題】膜の強度が高く、基体との密着性にも優れた防曇膜の提供。

【解決手段】基体1上に一次元的に成長した多数の柱状相2と、それを取り囲むマトリックス相3とからなる複合膜4中の、柱状相2を除去することにより形成され、膜の一方の表面から他方の表面まで連続する壁で取り囲まれた一次元的に貫通する多数の気孔を有し、水に対する接触角が30°以下である、防曇膜5。



## 【特許請求の範囲】

【請求項1】基体上に一次元的に成長した多数の柱状相と、それを取り囲むマトリックス相とからなる複合膜中の、一次元的に成長した柱状相を除去することにより形成された、膜の一方の表面から他方の表面まで連続する壁で取り囲まれた一次元的に貫通する多数の気孔を有する防曇膜であって、水に対する接触角が $30^\circ$ 以下であることを特徴とする防曇膜。

【請求項2】前記防曇膜が、酸化物、炭化物、ホウ化物、窒化物および金属から選ばれた1種以上からなる請求項1に記載の防曇膜。

【請求項3】前記一次元的に貫通する気孔の平均孔径が $1\sim 500\text{nm}$ である請求項1または2に記載の防曇膜。

【請求項4】前記防曇膜の比表面積が $20\sim 2000\text{m}^2/\text{g}$ である請求項1、2または3に記載の防曇膜。

【請求項5】基体上に、請求項1、2、3または4に記載の防曇膜を有する防曇膜付き基体。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、一次元的に貫通する気孔（以下、一次元貫通気孔ともいう）を持つ防曇膜に関する。詳しくは、窓ガラス、鏡または光学レンズ表面等の曇り防止用防曇膜として好適に利用でき、高耐久性を有する防曇膜に関する。

## 【0002】

【従来の技術】浴室や洗面台の鏡は水蒸気を多量に含む空気に触れると、表面に光の波長程度かそれ以上の大きさの水滴が付着し、その水滴によって光が乱反射され曇を生じる。また、外気で冷やされた建築物の窓ガラス内面、自動車などの風防ガラス内面または眼鏡の表面に、光の波長程度かそれ以上の大きさの水滴が付着し、その水滴によって光が散乱されると曇を生じる。これらは、本来透明であるべきガラス表面に微小な水滴が付着することによる。

【0003】この問題の根本的な原因は、鏡や窓に使われるガラスの表面が親水性と疎水性の中間の性質（純水の接触角で $50\sim 90^\circ$ 程度）を示し、液滴が半球状にガラス表面に付着することに起因する。このような問題は、ガラスのみならず水に対する濡れ性がガラスと同等である金属、セラミックスまたはある種のプラスチックでも同様に起こりうる。

【0004】このように表面が微小な液滴の付着によって曇る問題を解決するために、ガラスやプラスチックの表面に親水性の膜を形成し、水滴が付着しても半球状にならないようにすることで防曇性を発現させる方法などが提案されてきた。具体的には、A)ジメチルアルキルアンモニウムクロリドなどの有機カチオン界面活性剤でガラスやプラスチックの表面を親水化処理する方法、B)界面活性剤や酸化チタンを練り込んだ透明樹脂

フィルムをガラスやプラスチックの表面に貼り付ける方法などが提案されてきた。

【0005】また、C)ガラスやプラスチックなどの表面に多孔質の無機膜（アルミナやアルミナ-シリカ系など）を形成し、表面の凹凸によって親水性の向上を図る方法などが試みられてきた。

【0006】しかし、A)の方法においては、界面活性剤の付着力が弱いいため、窓ガラスや自動車の風防ガラスに用いた場合、すぐに界面活性剤成分が脱離して親水効果および防曇効果がなくなる問題があった。また、B)の方法では、界面活性剤成分が透明樹脂フィルムから溶出して親水効果が低減したり、透明樹脂フィルムが太陽光で劣化し透明性を失う問題があった。

【0007】C)の方法は、上記有機膜を用いる方法に比べてある程度耐久性の向上が期待できる。しかし、このような膜では、防曇効果を上げるため膜の気孔率を増加させると、膜そのものの強度、および、膜と基板との密着強度が低くなる、特性上相矛盾する問題が生じる場合が多かった。

【0008】また、通常、多孔質無機膜を形成する場合、シリカやアルミナなどの微粉末を含むセラミックスラリーを調整し、スラリーをディップ法やドクターブレード法などでガラスやプラスチックの表面に塗布した後に加熱、乾燥または焼結する方法が用いられるが、この方法で作られる膜では、膜中に含まれる気孔の気孔径を描えるのが難しく、数十 $\mu\text{m}$ の孔が必ず存在するのが通例である。このように大きな孔が膜表面に存在すると、この孔に空気中に浮遊するタバコのヤニや各種粉塵などの微粒子がはまりこみ簡単な洗浄ではこれらを取り除くことが困難になる問題があった。

## 【0009】

【発明が解決しようとする課題】本発明は、従来技術が有する前述の欠点を解消し、膜の強度が高く、基体との密着性にも優れる防曇膜および防曇膜付き基体の提供を目的とする。本発明はまた、汚れが落ちやすい前記防曇膜および防曇膜付き基体の提供を目的とする。

## 【0010】

【課題を解決するための手段】本発明は、基体上に一次元的に成長した多数の柱状相と、それを取り囲むマトリックス相とからなる複合膜中の、一次元的に成長した柱状相を除去することにより形成された、膜の一方の表面から他方の表面まで連続する壁で取り囲まれた一次元的に貫通する多数の気孔を有する防曇膜であって、水に対する接触角が $30^\circ$ 以下であることを特徴とする防曇膜を提供する。

【0011】本発明においては、マトリックス相が防曇膜を構成する材料となり、該マトリックス相は緻密質体である。本発明の防曇膜は、二段階のプロセスで形成される。すなわち、第一段階では、一次元的に成長した多数の柱状相と、それを取り囲むマトリックス相とからな

ピタキシー法などの物理的成膜法や、ゾル・ゲル法、スプレーパイロリシス法または塗布法などの溶液法、さらに、メッキ法など利用できる。このなかでもスパッタ法は緻密な膜を得やすいこと、基体との密着性が高い膜が得られることに加えて量産性や大面積成膜性に優れており、特に好ましい。

【0024】スパッタ法等によってアモルファス前駆体膜を形成する場合、柱状相を形成する材料と、マトリックス相を形成する材料を用いてターゲットを構成する方法としては、特に限定されないが、柱状相を形成する材料の粉末と、マトリックス相を形成する材料の粉末を混合したものをターゲットとすることができる。例えば、Fe-Si-O系のアモルファス前駆体膜を形成する場合、FeO粉末とSiO<sub>2</sub>粉末を混合したものをターゲットとして使用できる。

【0025】複合膜の第二形成方法において、最初に形成されるアモルファス前駆体膜に含まれる元素の組み合わせとしては、遷移金属とそれ以外の金属元素および酸素がある。遷移金属の例としては、熱処理後に、膜に含まれる他の金属と分離して別々の化合物相となるものであればよいが、熱処理時の取り扱いの容易さ等を考慮し、V、Cr、Mn、Ni、Fe、Co、Cu、Znなどの3d遷移金属や、これらの金属を主成分とする合金、その他の多価陽イオンCe、Nd、Sm、Erなどの希土類元素、から選ばれる1種以上が挙げられる。

【0026】遷移金属以外の金属元素としては、続いて行われる熱処理時に遷移金属と反応しないものであればよい。この金属元素は熱処理時に柱状相（遷移金属化合物針状結晶）を取り囲むマトリックス相となりエッチング後に一次元貫通気孔を持つ膜を構成する成分となるため、膜の利用目的によって選ばれる。例えば、Si、Al、Mg、Zr、Sn、Inなどが挙げられる。

【0027】アモルファス前駆体膜をスパッタ成膜する場合、後に行われる加熱処理によって一次元的に成長する柱状相の直径は、スパッタ時のArガス圧により変化する。例えばFe-Si-O系の膜の場合、2PaのArガス圧で製膜した膜を600℃で熱処理すると約4nmの直径のヘマタイト(Fe<sub>2</sub>O<sub>3</sub>)が析出するが、8PaのArガス圧で製膜した場合、同様の処理を行うと直径約20nmのヘマタイトが析出する。一次元貫通気孔の直径は一次元的に成長する柱状相の直径にほぼ一致するため、エッチング後に最終的に得られる本発明の防曇膜の一次元貫通気孔の平均孔径は、成膜条件（スパッタ時のArガス圧）によって、制御できる。

【0028】複合膜の第二形成方法においては、遷移金属とそれ以外の金属および酸素を含むアモルファス前駆体膜を加熱処理して、遷移金属酸化物とそれ以外の金属の酸化物が分離析出する、共晶分解反応を起こさせる。このアモルファス相からの二相析出は同時に、しかも膜表面から起こることが重要である。加熱するときの処理

条件としては共晶分解反応が起こる条件であればよい。すなわち、温度については、共晶分解反応が起こる温度でなおかつ反応が十分な速度で進行する温度であればよい。具体的には400～650℃程度の温度が好ましい。

【0029】共晶分解反応を引き起こすためには遷移金属の価数を変化させる必要がある。この方法としてアモルファス前駆体膜を酸化性の雰囲気中で処理する場合と還元性の雰囲気中で処理する方法の2つが可能である。酸化物の共晶反応の場合、還元雰囲気中で処理すると不均一核形成して均一な共晶組織が形成されない場合がある。この場合には酸化雰囲気下で熱処理することにより均一な共晶組織を形成できる。

【0030】第二段階では、第一段階で形成された複合膜から、一次元的に伸びた柱状相のみを酸やアルカリを用いて選択的にエッチングし、取り除く。このエッチング処理で用いる酸としては硫酸、塩酸、硝酸、シュウ酸、酢酸など、柱状相のみを選択的に取り除くのに適したものが選ばれる。例えば、複合膜の第一形成方法によって作製された金属コバルト・シリカ複合膜から金属コバルトを取り除くには0.1mol/Lの硝酸水溶液で数分間処理するだけで金属コバルトのみを完全に除去できる。

【0031】また、複合膜の第二形成方法によって形成されたFe-Si-O系の複合膜の場合、一次元的に伸びたヘマタイトは塩酸の水溶液に可溶であるのに対して、シリカは同溶液に不溶であるため、約6mol/Lの塩酸水溶液に膜を浸漬することにより選択エッチングできる。

【0032】本発明の防曇膜は、上述のようにして形成されたものであり、膜の一方の表面から他方の表面まで連続する壁で取り囲まれた一次元的に貫通する多数の気孔を有する防曇膜であって、水に対する接触角が30°以下の膜である。水に対する接触角が30°超では、十分な防曇効果が得られない。

【0033】本発明の防曇膜は、酸化物、炭化物、ホウ化物、窒化物および金属から選ばれた1種以上からなり、用途に応じて選択されるが、耐久性、強度、化学的安定性、形成しやすさ等の観点から、酸化物が最も好ましい。また、防曇性の観点からはシリカが好ましい。

【0034】また、本発明の防曇膜における、一次元的に貫通する気孔の平均孔径は、1～500nmであることが好ましい。1nm未満では、十分な防曇効果が得られず、また、500nm超では、十分な防曇効果が得られないうえに、膜の強度または基体との密着性も低下する可能性がある。

【0035】さらに、本発明の防曇膜の比表面積は、20～2000m<sup>2</sup>/gであることが好ましい。20m<sup>2</sup>/g未満では、十分な防曇効果が得られず、また、2000m<sup>2</sup>/g超では、十分な膜強度が得られない可能性が

ある。

【0036】本発明はまた、基体上に、前記防曇膜を有する防曇膜付き基体を提供する。本発明の防曇膜を形成する基体としては、複合膜の第一形成方法を用いる場合は、ガラス、セラミックス、金属、プラスチック等の基板またはフィルムを使用でき、また、複合膜の第二形成方法を用いる場合は、ガラス、セラミックス、耐熱金属等の基板またはフィルムを使用できる。

【0037】耐熱金属としてはFe、Ni、Cr、Vなどからなるステンレス鋼やハステロイなどの耐酸化性の合金が好適である。また、本発明の防曇膜を、多孔質セラミック基板等の、表面に凹凸を有する基体上に形成する場合、表面の凹凸があまり激しくなければ、第一形成方法による複合膜、または、第二形成方法によるアモルファス前駆体膜を直接形成すればよい。基体表面の凹凸が激しく第一段階の膜の直接形成が難しい場合には、基体表面の凹凸を、樹脂その他の材料で充填したのち表面を研磨して平滑にし、平滑な基体表面上に本発明の防曇膜を形成すれば、充分な密着強度を確保できる。本発明の防曇膜は様々な組成で構成できる。本発明の防曇膜は、車両の風防ガラス、建築物の窓ガラス、鏡、光学レンズ等に使用される防曇膜などに好適である。

【0038】

【作用】本発明の防曇膜は、膜表面から連続する気孔が膜内部まで存在することから、表面に付着した水滴が膜内部まで浸透し実用上防曇効果を示す程度に高い親水性を有する。

【0039】さらに、本発明の防曇膜は一次元の貫通気孔のまわりを連続したマトリックス相が取り囲んでいるため、従来からある多孔質無機膜に比べて原理的に膜強度が大きく、基体との密着性も良い。膜強度が大きいことは、従来の多孔質無機防曇膜がセラミック粒子を焼結などで緩く結合したものであるのに対して、本発明の膜では一次元貫通気孔を取り囲むマトリックスが完全に連続した一体成形物であることによる。

【0040】また、基板との密着性についても、第一段階の複合膜（第二形成方法によるアモルファス前駆体膜を含めて）をスパッタ法等で形成すれば特に密着性の高い膜が得られる。また、従来の多孔質無機膜は、防曇効果を上げるため膜の気孔率を増加させると、膜そのものの強度、および、膜と基板との密着強度が低くなる、特性上相矛盾する問題が生じる場合が多かったが、本発明の防曇膜では、高い防曇効果を維持しつつ、膜の強度と、基板との密着性を、両方とも高くすることができ、防曇性と高耐久性を有する防曇膜を実現できる。

【0041】

【実施例】（実施例1）複合膜の第一形成方法を用いて、厚さ1.2mmのソーダライムガラス基板上に金属CoとSiO<sub>2</sub>の2相からなる複合膜を形成した。スパッタに際しては、直径15.24cmの金属Coターゲット

ットの上に5mm角のSiO<sub>2</sub>チップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち20%を占めるようにSiO<sub>2</sub>チップの量を調節した。真空槽を5×10<sup>-4</sup>Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2Paになるように流量調節し600Wの高周波入力によりプラズマを発生させた。成膜速度は約0.25nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。なお、基板周辺部は、マスクを施して、膜を形成しなかった。

【0042】このようにして形成したCo-SiO<sub>2</sub>複合膜をTEM（透過型電子顕微鏡）で観察した結果、平均粒径約10nmのCo結晶粒子が柱状に成長しており、そのまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいることが確認された。

【0043】第二段階として、上記の方法で形成した膜厚500nmのCo-SiO<sub>2</sub>複合膜を0.1mol/Lの硝酸水溶液に5分間浸漬してエッチングを行った。Co-SiO<sub>2</sub>複合膜からCoの柱状相をエッチングにより取り除いた後の膜をSEM（走査型電子顕微鏡）で観察した結果、Co柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留していることが確認された。

【0044】図2は、以上のようにして形成された防曇膜の液体窒素温度での等温吸脱着曲線である。図から、差圧(P/P<sub>0</sub>)=0.6付近で明瞭な窒素ガスの吸着・脱離が見られ、得られた防曇膜が直径10nm程度の細孔を多数有し、孔の内壁の比表面積が約1000m<sup>2</sup>/g（活性炭に相当する程度）であることがわかる。

【0045】また、得られた防曇膜の表面に直径約1mmの純水の水滴を滴下して接触角を測定したところ約15°であった。また、得られた防曇膜を基板ごと冷蔵庫に入れ1時間保持し5℃程度に冷やした後に、取り出して呼気を吹きかけたところ、膜のある部分には曇が生じないのに対して、膜のないガラス表面には微小な水滴が付着して曇が生じ不透明になった。

【0046】上述の防曇膜の耐久性を、テーパー耐摩耗性試験により調べたところ、1000回転しても水の接触角、防曇性能、透明性等に変化は見られなかった。なお、テーパー耐摩耗性試験は、市販のCS10型テーパー摩耗輪とJIS R6252に規定するAA180番の研磨紙と同等の品質の研磨紙を用い、500gの荷重をかけ、60rpmで1000回転して膜を摩耗させることによって行った。以下の例におけるテーパー耐摩耗性試験も同様である。

【0047】（比較例1）ポリスチレン微粒子（平均粒径0.06μm）を分散させたエチルシリケート水溶液に塩酸を加えて粘度調整したコーティング液を、ソーダライムガラス基板表面に塗布した後、約400℃に加熱し、膜厚500nmの多孔質シリカ膜を形成した。実施例1と同様のテーパー耐摩耗性試験により耐久性を調

べたところ、1000回では、膜が一部剥離し、透明性が損なわれた。

【0048】(実施例2) 成膜速度を約0.3nm/secとしたこと以外は、実施例1と同様に、膜厚500nmのCo-SiO<sub>2</sub>複合膜を形成した。このCo-SiO<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径が約20nmと大きくなっていることがわかった。

【0049】上記の方法で作製した膜厚500nmの試料を0.1mol/Lの硝酸水溶液に5分間浸漬してCo柱状相を溶解除去した。実施例1と同様にCo柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000m<sup>2</sup>/gおよび13°であり、呼気を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0050】(実施例3) 実施例1と同様の複合ターゲットを用い、次のようにして、厚さ1.2mmのソーダライムガラス基板上に、Co-SiO<sub>2</sub>複合膜を形成した。すなわち、真空槽を5×10<sup>-4</sup>Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が8Paになるように流量調節し800Wの高周波入力によりプラズマを発生させた。成膜速度は約0.6nm/secであり、成膜時に基板温度を200℃に加熱した。

【0051】このCo-SiO<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径が約100nmと大きくなっていることがわかった。

【0052】上記の方法で作製した膜厚1500nmの試料を0.1mol/Lの硝酸水溶液に15分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000m<sup>2</sup>/gおよび12°であり、呼気を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0053】(実施例4) 実施例1と同様の複合ターゲットを用い、次のようにして、厚さ2mmの Hastelloy 板上に、Co-SiO<sub>2</sub>複合膜を形成した。すなわち、真空槽を5×10<sup>-4</sup>Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2Paになるように流量調節し400Wの高周波入力によりプラズマを発生させた。成膜速度は約0.35nm/secであり、成膜時には意図的な基板温度やバイアス印加は行わなかった。

【0054】このCo-SiO<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co

結晶粒子の柱状相のまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約10nmであった。この方法で作製した膜厚800nmの試料を0.1mol/Lの硝酸水溶液に10分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000m<sup>2</sup>/gおよび12°であり、呼気を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0055】(実施例5) 実施例1と同様の複合ターゲットを用い、次のようにして、厚さ5mmのアルミナセラミックス基板上に、Co-SiO<sub>2</sub>複合膜を形成した。すなわち、真空槽を5×10<sup>-4</sup>Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2Paになるように流量調節し400Wの高周波入力によりプラズマを発生させた。成膜速度は約0.3nm/secであり、成膜時には意図的な基板温度やバイアス印加は行わなかった。

【0056】このCo-SiO<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約9nmであった。この方法で作製した膜厚700nmの試料を0.1mol/Lの硝酸水溶液に10分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000m<sup>2</sup>/gおよび16°であり、呼気を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0057】(実施例6) 実施例1と同様の複合ターゲットを用い、次のようにして、厚さ1.8mmのポリエチレンフィルムシート上に、Co-SiO<sub>2</sub>複合膜を形成した。すなわち、真空槽を5×10<sup>-4</sup>Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2Paになるように流量調節し400Wの高周波入力によりプラズマを発生させた。成膜速度は約0.2nm/secであり、成膜時には意図的な基板温度やバイアス印加は行わなかった。

【0058】このCo-SiO<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのSiO<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約15nmであった。この方法で作製した膜厚200nmの試料を0.1mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、SiO<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000m<sup>2</sup>/gおよび28°であり、

呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0059】(実施例7) エポキシ樹脂を厚さ2mmの多孔質シリカプレート上に塗布し、硬化させたのち、基板表面をダイヤモンド研磨装置で研磨し、平滑な研磨面を得た。この基板上に、実施例1と同様の複合ターゲットを用い、次のようにして、 $\text{Co-SiO}_2$ 複合膜を形成した。すなわち、真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し400Wの高周波入力によりプラズマを発生させた。成膜速度は約0.35 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0060】この $\text{Co-SiO}_2$ 複合膜内部の構造は、実施例1で得られた $\text{Co-SiO}_2$ 複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスの $\text{SiO}_2$ マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約9 nmであった。この方法で作製した膜厚300 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、 $\text{SiO}_2$ マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび8°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0061】(実施例8) 厚さ1.2 mmのソーダライムガラス上に、次のようにして、 $\text{Co-TiO}_2$ 複合膜を形成した。スパッタに際しては、直径15.24 cmの金属Coターゲットの上に0.5 mm角の $\text{TiO}_2$ チップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち30%を占めるように $\text{TiO}_2$ チップの量を調節した。真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し400Wの高周波入力によりプラズマを発生させた。成膜速度は約0.4 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0062】この $\text{Co-TiO}_2$ 複合膜内部の構造は、実施例1で得られた $\text{Co-SiO}_2$ 複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスの $\text{TiO}_2$ マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約8 nmであった。この方法で作製した膜厚250 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、 $\text{TiO}_2$ マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび28°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0063】また、エッチング後に得られたアモルファ

スの $\text{TiO}_2$ 膜を空气中600℃で1時間加熱したところ、結晶質のアナターゼに変化し、なおかつ膜の比表面積がほとんど変化していなかった。

【0064】(実施例9) 厚さ1.2 mmのソーダライムガラス上に、次のようにして、 $\text{Co-SiC}$ 複合膜を形成した。スパッタに際しては、直径15.24 cmの金属Coターゲットの上に0.5 mm角のSiCチップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち40%を占めるようにSiCチップの量を調節した。真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し800Wの高周波入力によりプラズマを発生させた。成膜速度は約0.3 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0065】この $\text{Co-SiC}$ 複合膜内部の構造は、実施例1で得られた $\text{Co-SiO}_2$ 複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのSiCマトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約6 nmであった。この方法で作製した膜厚250 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、SiCマトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび28°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0066】(実施例10) 厚さ1.2 mmのソーダライムガラス上に、次のようにして、 $\text{Co-Si}_3\text{N}_4$ 複合膜を形成した。スパッタに際しては、直径15.24 cmの金属Coターゲットの上に0.5 mm角の $\text{Si}_3\text{N}_4$ チップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち40%を占めるように $\text{Si}_3\text{N}_4$ チップの量を調節した。真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し800Wの高周波入力によりプラズマを発生させた。成膜速度は約0.3 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0067】この $\text{Co-Si}_3\text{N}_4$ 複合膜内部の構造は、実施例1で得られた $\text{Co-SiO}_2$ 複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスの $\text{Si}_3\text{N}_4$ マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約6 nmであった。この方法で作製した膜厚250 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、 $\text{Si}_3\text{N}_4$ マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび28°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇

効果があることが確認された。

【0068】(実施例11) 厚さ1.2mmのソーダライムガラス上に、次のようにして、Co-Cr複合膜を形成した。スパッタに際しては、直径15.24cmの金属Coターゲットの上に0.5mm角のCrチップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち40%を占めるようにCrチップの量を調節した。真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し800Wの高周波入力によりプラズマを発生させた。成膜速度は約0.3 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0069】このCo-Cr複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co柱状結晶粒子(柱状相)のまわりを、Cr結晶集合体からなるマトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約6 nmであった。この方法で作製した膜厚250 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、Crマトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび28°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0070】(実施例12) 厚さ1.2mmのソーダライムガラス上に、次のようにして、Co-ZrB<sub>2</sub>複合膜を形成した。スパッタに際しては、直径15.24cmの金属Coターゲットの上に1cm角のZrB<sub>2</sub>セラミックスチップを置いた複合ターゲットを用いた。ターゲットの片面の全表面積のうち40%を占めるようにZrB<sub>2</sub>セラミックスチップの量を調節した。真空槽を $5 \times 10^{-4}$  Paまで排気したのちにArガスを導入し、真空槽内部のガス圧が2 Paになるように流量調節し600Wの高周波入力によりプラズマを発生させた。成膜速度は約0.38 nm/secであり、成膜時には積極的な基板加熱や基板バイアス印加は行わなかった。

【0071】このCo-ZrB<sub>2</sub>複合膜内部の構造は、実施例1で得られたCo-SiO<sub>2</sub>複合膜と同様に、Co結晶粒子の柱状相のまわりをアモルファスのZrB<sub>2</sub>マトリックス相が取り囲んでいるが、この場合にはCo結晶の平均粒子径は約10 nmであった。この方法で作製した膜厚450 nmの試料を0.1 mol/Lの硝酸水溶液に5分間浸漬してCo粒子を溶解除去した。実施例1と同様に、Co柱状相が溶出し、ZrB<sub>2</sub>マトリックス相が残留した。膜の比表面積、純水に対する接触角は、それぞれ約1000 m<sup>2</sup>/gおよび22°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0072】(実施例13) 厚さ1.0mmの耐熱ガラ

ス(コーニング#7059)基板上にFe-Si-Oの三成分からなるアモルファス前駆体膜をスパッタ法で形成した。スパッタには、Fe<sub>3</sub>O<sub>4</sub>粉末とSiO<sub>2</sub>粉末をそれぞれ体積比で70%および30%の割合で混合し焼結したものをターゲットに用いた。真空槽を $5 \times 10^{-4}$  Paまで排気した後にアルゴンガスを導入し、真空槽内部のガス圧が2 PaとなるようにArガスの流量を調節し、4.4 W/cm<sup>2</sup>の高周波を入力してプラズマを発生させた。このときの成膜速度は約0.2 nm/secであった。

【0073】成膜したアモルファス前駆体膜をSEMで観察したところ、ガラス基板上に厚さ約120 nmのアモルファス膜が形成されていた。アモルファス膜中にはクラックやボアなどの欠陥が見られず、非常に緻密な膜が形成されていた。引き続き、このアモルファス膜を空气中600℃で2時間、加熱処理した。加熱処理によって形成されたFe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>複合膜をTEMで観察したところ、一次元的に伸びた針状のヘマタイト(Fe<sub>2</sub>O<sub>3</sub>)結晶とそのまわりを取り囲むシリカ(SiO<sub>2</sub>)が共晶組織を形成していることが確認された。ヘマタイト結晶は膜表面から基板との界面に向かって膜表面に垂直に伸びており、その直径は約4 nmであった。

【0074】最後に、上記の方法で熱処理した膜を基板ごと約6 mol/Lの塩酸水溶液に室温で48時間浸漬し、ヘマタイトのみ取り除いた。ヘマタイトを取り除いてできた防曇膜の断面をTEMで観察すると、アモルファスのシリカマトリックスと一次元的に伸びる貫通気孔が観察された。貫通気孔の直径は、酸処理前のヘマタイトの直径とほぼ同じ4 nmであり、該貫通気孔がシリカ膜中に存在することが確認された。膜の比表面積、純水に対する接触角は、それぞれ約800 m<sup>2</sup>/gおよび8°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0075】(実施例14) 厚さ1.0mmの耐熱ガラス(コーニング#7059)基板上にFe-Si-Oの三成分からなるアモルファス前駆体膜をスパッタ法で形成した。スパッタには、Fe<sub>3</sub>O<sub>4</sub>粉末とSiO<sub>2</sub>粉末をそれぞれ体積比で70%および30%の割合で混合し焼結したものをターゲットに用いた。真空槽を $5 \times 10^{-4}$  Paまで排気した後にアルゴンガスを導入し、真空槽内部のガス圧が8 PaとなるようにArガスの流量を調節し、4.4 W/cm<sup>2</sup>の高周波を入力してプラズマを発生させた。このときの成膜速度は約0.1 nm/secであった。

【0076】成膜したアモルファス前駆体膜をSEMで観察したところ、ガラス基板上に、厚さ約80 nmで、実施例13とほぼ同様のアモルファス膜が形成されていた。アモルファス膜中にはクラックやボアなどの欠陥が見られず、非常に緻密な膜が形成されていた。引き続き、このアモルファス膜を空气中600℃で2時間、加

熱処理した。加熱処理によって形成された $\text{Fe}_2\text{O}_3-\text{SiO}_2$ 複合膜をTEMで観察したところ、実施例13と同様に、一次元的に伸びた針状のヘマタイトとそのまわりを取り囲むシリカが共晶組織を形成していた。ヘマタイト結晶は膜表面から基板との界面に向かって膜表面に垂直に伸びており、その直径は約20nmであった。

【0077】最後に、上記の方法で熱処理した膜を基板ごと約6mol/Lの塩酸水溶液に室温で48時間浸漬し、ヘマタイトのみ取り除いた。膜断面の微細組織をTEMで観察したところ、酸処理前のヘマタイトの直径とほぼ同じ直径の貫通気孔がシリカ膜中に存在することが確認された。膜の比表面積、純水に対する接触角は、それぞれ約1200 $\text{m}^2/\text{g}$ および5°であり、呼吸を吹きかける実験により実施例1とほぼ同等の防曇効果があることが確認された。

【0078】(比較例2)実施例13において得られたアモルファス前駆体膜を、空气中800℃で1時間、加熱処理した。加熱処理後の膜をTEMで観察した結果、ヘマタイト結晶は針状ではなく直径約10nmの球状でありシリカマトリックスに包まれるように析出していた。引き続き、上記の方法で熱処理した膜を基板ごと約6mol/Lの塩酸水溶液に浸漬したが、100時間後にも全てのヘマタイト結晶を取り除くことはできなかった。

【0079】

【発明の効果】本発明の防曇膜は、膜の一方の表面から他方の表面まで連続する壁で取り囲まれた一次元的に貫通する多数の気孔を有しているため、高い防曇性能を保持しつつ、膜の強度が高く、基体との密着性にも優れている。また、本発明の防曇膜は、多種類の基体に適用で

き、様々な組成で構成できる。

【0080】また、本発明の防曇膜に含まれる気孔の直径は1~500nm程度でほぼ揃っており、数十 $\mu\text{m}$ 程度の巨大な孔は存在しない。したがって、空气中に浮遊するタバコのヤニや各種粉塵などの微粒子がはまりこむことがなく、簡単な洗浄でこれらを取り除くことができる。

【0081】本発明の防曇膜が、酸化物、炭化物、ホウ化物、窒化物を主成分とする場合には、鏡、建築用窓ガラス、自動車の風防ガラス、または光学レンズ表面等の曇り防止用防曇膜などに好適である。また、Cr、Ni、Cu、Au、Al、Ptなどの金属を主成分とする場合は、反射鏡、カーブミラーの表面コート、赤外線反射用コーティング用の防曇膜などに好適である。

【0082】本発明の防曇膜は、表面から膜内部まで貫通する気孔を持ち、大きな比表面積を持つことから、触媒機能および触媒担持機能を付加して表面に付着した有機物を光分解するなどにより、防汚機能を付加し、防曇性が永続する膜とすることもできる。

【図面の簡単な説明】

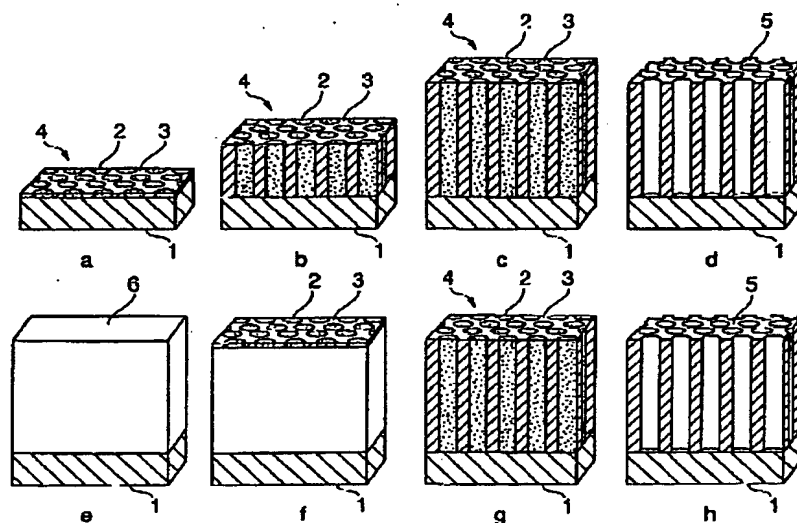
【図1】本発明の防曇膜を形成する手順を示す模式図。

【図2】実施例1の防曇膜の液体窒素温度での等温吸脱着曲線。

【符号の説明】

- 1：基体
- 2：柱状相
- 3：マトリックス相
- 4：複合膜
- 5：本発明の防曇膜
- 6：アモルファス前駆体膜

【図1】



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